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(71)Applicant : ASAHI CHEM IND CO LTD
(72)Inventor : KANEKO MASAMICHI
TANI SHIGENARI

(54) PRODUCTION OF FOAMABLE RESIN PARTICLE

(57)Abstract:
PROBLEM TO BE SOLVED: To produce the above spherical particle in excellent productivity in a short impregnation time of a blowing agent without causing blocking, by impregnating a specific polystyrene-based resin particle with the blowing agent.
SOLUTION: In obtaining the above particle having ≥0.5mm and ≤3.0mm average particle diameter by impregnating (A) a conjugated diene-based polymer component-containing polystyrene-based resin particle with (B) a blowing agent, a particle which is obtained by melting the component A in an extruder by heating, extruding the melt from an extrusion die at 2,500-10,000 (1/second) shear rate and 150-700 poise apparent viscosity of the resin at a die land part into water and simultaneously cutting by a die face is used as the resin particle before impregnation with the component B. Preferably the content of the conjugated diene component of the component A is 3-20wt.%, the intrinsic viscosity of the polystyrene-based component phase at 30° C is 0.6-0.9 and the sphericity of the objective particle is preferably 1.0-1.

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Claims

1. A method for producing a spherical expandable polystyrene-based resin particle having an average diameter of 0.5 to 3.0 mm by impregnating a polystyrene-based resin particle containing conjugated diene-based polymer component with a blowing agent in an aqueous medium,
wherein a particle obtained by heat-melting the polystyrene-based resin particle containing conjugated diene-based polymer component in an extruder, extruding the melt from an extrusion die into water at a shear rate of 2,500 to 10,000 (1/sec) and an apparent viscosity of the resin of 150 to 700 poise at a die land part and simultaneously cutting by a die face is used as the resin particle before impregnation with the blowing agent.

2. The method for producing a spherical expandable polystyrene-based resin particle according to Claim 1, wherein the content of polystyrene-based resin containing conjugated diene-based polymer component is 3 to 20 wt %, and the intrinsic viscosity of the polystyrene-based component phase at 30 deg. C in toluene is 0.6 to 0.9.

3. The method for obtaining a spherical expandable polystyrene-based resin particle according to Claim 1, wherein the sphericity of the expandable polystyrene-based resin particle is 1.0 to 1.3.

Description

[0001] The present invention relates to a method for obtaining a polystyrene-based expandable particle, more particularly to a method for obtaining a polystyrene-based expandable particle containing conjugated diene-based polymer component which has an improved productivity in the process of impregnating with a blowing agent.

Field of the invention

Background Art

[0002] Recently, a molded foamed article of expandable particles comprising a polystyrene-based resin containing conjugated diene-based polymer component is attracting attention as a polystyrene-based molded foamed article that excels in crack resistance. Among such expandable particles of polystyrene-based resin containing conjugated diene-based polymer component, a particle having higher sphericity is easy to fill in the

mold, which will help fusing particles with each other and improve crack resistance.

[0003] In Japanese Patent Application Laid-Open Nos. H6-49262 and H7-90105, it is disclosed that a high impact polystyrene obtained by polymerization of a polybutadiene and a styrene-based monomer is extruded from an extruder into the form of strand and then cut with a cutter to become a cylindrical resin particle, which is to be impregnated with a blowing agent in an aqueous medium to produce an expandable resin particle. However, there is a problem that since this particle is in the cylindrical shape before the impregnation with the blowing agent, it takes a long time to deform the particle into the sphere shape by heating and plasticizing the resin in the process of impregnating with the blowing agent.

[0004] Thus, it is advantageous to preform the particle into the sphere instead of the cylindrical shape before the impregnation. A method for producing an expandable styrene-based resin particle has been known, in which a styrene-based resin is heat-melted in an extruder to be extruded from a die nozzle and hot-cut simultaneously to make a particle in the substantially spherical form, and the particle is then impregnated with a blowing agent in an aqueous medium.

[0005] Japanese Patent Publication No. S58-33889 discloses a method for producing an expandable polystyrene particle, in which polystyrene is extruded with a die temperature of 230 to 240 deg. C and hot-cut in water to produce generally spherical polystyrene particles, and the particles are then dispersed in an aqueous medium with polyvinyl alcohol dissolved therein to be impregnated with cyclohexane and thereafter with n-pentane. However, a problem has been found that with the use of polystyrene containing conjugated diene-based polymer component as an alternative of polystyrene, the particles obtained by hot-cutting in water is likely to become flattened in the process of impregnation of the blowing agent and fail to become spherical.

[0006] In Japanese Patent Application Laid-Open Nos. H4-325534 and H6-145409, it is also disclosed a method for producing an expandable styrene-based resin particle. In order to recycle a waste molded article of the

expandable polystyrene-based resin, the waste molded article of the expandable polystyrene-based resin is crushed and heat-melted in an extruder to give cylindrical particles, which are then fed into the extruder again to be extruded from a die nozzle and hot-cut simultaneously to give spherical resin particles. The obtained particles are further impregnated with a blowing agent in an aqueous medium. However, there is a problem that with the use of polystyrene resin containing conjugated diene-based polymer component as an alternative of the recycled expandable polystyrene resin, the particles obtained by hot-cut are likely to have various forms, taking a long time to deform into the sphere shape by heating and plasticizing the particle in the process of impregnation of the blowing agent. In addition, blocking of particles may occur during impregnation if the impregnation temperature is increased so as to shorten the length of time taken for impregnation.

Problems to be solved

[0007] The present invention is intended to solve the above described problems and provides a method for producing an expandable polystyrene resin particle containing conjugated diene-based polymer component, in which polystyrene resin particles containing conjugated diene-based polymer component are impregnated with a blowing agent in a aqueous medium, while blocking of the particles is suppressed, and the particles are deformed into the sphere shape within a short length of time.

Means for solving the problems

[0008] The present invention relates to a method for obtaining a spherical expandable polystyrene-based resin particle having an average diameter of 0.5 to 3.0 mm by impregnating a polystyrene-based resin particle containing conjugated diene-based polymer component with a blowing agent in an aqueous medium, wherein a particle obtained by heat-melting the polystyrene-based resin particle containing conjugated diene-based polymer component in an extruder, extruding the melt from an extrusion die into water at a shear rate of 2,500 to 10,000 (1/sec) and an apparent viscosity of the resin of 150 to 700 poise at a die land part and simultaneously cutting by a die face is used as the resin particle before

impregnation with the blowing agent.

[0009] The polystyrene-based resin containing conjugated diene-based polymer component of the present invention includes 3 to 20 wt % of conjugated diene component, and has the intrinsic viscosity of the polystyrene-based component phase at 30 deg. C in toluene of 0.6 to 0.9. Further, the sphericity of the expandable polystyrene-based resin particle of the present invention is 1.0 to 1.3.

[0010] The present invention differs from the prior art in that the expandable particle is made from a spherical particle obtained by hot-cutting the resin in the water with the shear rate of the resin at the die land being 2,500 to 10,000 (1/sec.) and the apparent viscosity of the resing being 150 to 700 poise.

[0011] Fig. 1 and Fig. 2 are schematic diagrams showing an extruder and a device for underwater hot-cut. A heat-melted resin having been kneaded with a screw (8) of the extruder is fed into a die land (10) provided in a die head (1) of the extruder and extruded from an extruding hole (12) into a cutter box (5). Inside the cutter box, water is circulated. The hot-cutting the resin in the water is a method of cutting the resin at a die face (9) with a cutting blade (3) being rotated rapidly by a motor (4) immediately after the resin being extruded from the extruding hole, and evacuating the cut resin particle with the circulating water from the cutter box (5).

[0012] Next, a mechanism of obtaining a spherical particle by hot-cut of the extruded resin by the die face will be explained with reference to the figures. As for flowage of the resin inside the die land (10), a flow velocity distribution is generated by shear stress caused by the wall surface, so that the flow velocity is large in the central portion of the land, while the flow velocity is small on the wall surface of the land. Accordingly, after the cutting blade (3) has passed the die face (9) (thus, a front cut surface is formed), the resin is extruded in such a way that the central portion thereof is raised, whose surface is then cooled off by water. The front cut surface becomes rounded in this way. The resin that is seen from the extruding hole with the raised central portion is further cut by the cutting blade approaching again (thus, a rear cut surface is formed), to

make a particle. After the particle is produced, the rear cut surface is raised and rounded in its central portion by the surface tension of the resin. The particle is then further cooled off on the whole surface to become a solidified spherical particle.

[0013] Consequently, in forming the hot-cut particle into the spherical shape and preventing the particle from becoming oriented, the shear rate in the die land and the apparent viscosity of the resin, as well as flow characteristics of the resin, are the key factors. Also, among the resin characteristics, the viscosity in the polystyrene-based component phase as a matrix phase is important.

[0014] However, in the case of hot-cutting the polystyrene-based resin containing conjugated diene-based polymer component, it is difficult to form the particle into the spherical shape even if hot-cut is carried out under the same conditions as in the case of hot-cutting the polystyrene resin to obtain a particle having the generally spherical shape. This is partly because the flow characteristics of the polystyrene-based resin containing conjugated diene-based polymer component are different from those of the polystyrene resin. Also, remaining stress inside the particle or on the cut surface in hot-cut, the molecular orientation of the polystyrene-based component phase and the relaxation characteristic of molecular orientation by heat of the polystyrene-based component phase are affected by the conjugated diene-based polymer component to become different from those of the polystyrene-based resin alone.

[0015] In producing a spherical expandable particle of polystyrene-based resin containing conjugated diene-based polymer component, the productivity in the process of impregnation of the blowing agent depends upon how short a time it takes to form the particle into the spherical shape while impregnating with the desired amount of blowing agent and yet inhibiting blocking of the particles. According to the present invention, by using a particle obtained by hot-cutting the polystyrene-based resin containing conjugated diene-based polymer component in the water, it is possible in the process of impregnating with the blowing agent to shorten the amount of time required for the particle becoming spherical under the

influence of surface tension under the heat-plasticized condition and to improve the productivity.

[0016] In the case of impregnating a cylindrical particle of polystyrene-based resin containing conjugated diene-based polymer component with a blowing agent, orientation is relaxed and the particle comes to have a shape of a rugby ball as impregnation progresses to plasticize the resin. The particle becomes further flattened with heat, finally becoming spherical after a long period of time. Thus, it takes a long time to form the cylindrical particle into spherical shape, which means low productivity. In addition, blocking of the particles may easily occur if the impregnation temperature is increased to shorten the impregnation time.

[0017] In the present invention, the preferable range of the shear rate of the resin at the die land is from 2,500 to 10,000 (1/sec). When the shear rate is smaller than 2,500 (1/sec), the particle may has an irregular shape, which needs a longer time to form the particle into the spherical shape in impregnation of the blowing agent. When the shear rate is larger than 10,000 (1/sec), on the other hand, the particle may easily adhere to each other due to sticking and unsuccessful cutting. Further, internal stress of the particle and molecular orientation of the polystyrene-based component phase increase during the hot-cut, so that the particle gets flattened to have a shape of a rugby ball in impregnation of the blowing agent, which needs a longer time to form the particle into the spherical shape. The more preferable range of the shear rate is from 3,000 to 7,000 (1/sec).

[0018] The preferable range of the apparent viscosity is from 150 to 700 poise. When the apparent viscosity is smaller than 150 poise, the particles may be unsuccessfully cut to adhere to each other. When the apparent viscosity is larger than 700 poise, the particles are difficult to have a spherical shape. The more preferable range of the apparent viscosity is from 200 to 500 poise.

[0019] Although among methods of extrusion hot-cut of heat-melted resin are hot-cut in the air and water spraying hot-cut as well as the hot-cut in the water, the present invention employs the hot-cut in the water method, which has superior efficiency of heat transfer for cooling off the surface of

the extruded resin so as to form the particle into sphericity.

[0020] The polystyrene-based resin containing conjugated diene-based polymer component of the present invention includes a polystyrene resin or a copolymer including at least 50 parts of styrene monomers and another polymerizable monomer having been polymerized or copolymerized with a conjugated diene compound. The copolymerizable monomers may be methylstyrene, acrylonitrile, ester of acrylic acid or methacrylic acid and alcohol having the carbon number of 1 to 8, maleic acid, maleic anhydride and the like.

[0021] The content of conjugated diene component in the polystyrene-based resin containing conjugated diene-based polymer of the present invention preferably ranges from 3 wt % to 20 wt %. When the content is smaller than 3 wt %, the molded foamed article has an insufficient crack-resistant property. When the content is larger than 20 wt %, the strength of the molded foamed article will decrease.

[0022] The method for including conjugated diene-based polymer component in the polystyrene-based resin may be (1) a method of polymerizing a solution of a conjugated diene-based polymer dissolved in a styrene-based monomer to put the conjugated diene-based polymer in a continuous phase of the polystyrene-based resin as a disperse phase or (2) a method of mechanically mixing the polystyrene-based resin with conjugated diene-based polymer component, both of which can be used in the present invention.

[0023] The preferable range of limiting viscosity of the polystyrene-based component phase in the polystyrene-based resin containing conjugated diene-based polymer component of the present invention at 30 deg. C in toluene is from 0.6 to 0.9. When the limiting viscosity is smaller than 0.6, flowability of the resin is so large that the front cut surface of the extruded resin may be easily deformed in an irregular shape and fail to become rounded during the hot-cutting in the water. On the other hand, when the limiting viscosity is larger than 0.9, the rounded shape of the rear cut surface of the resin, which is obtained by the surface tension, is difficult to form, failing to make a spherical particle. Further, plasticization of the

resin in the process of impregnating with the blowing agent is inhibited, failing to form the particle into the spherical shape.

[0024] The conjugated diene-based polymers of the present invention may be polybutadiene, polyisoprene, styrene-butadiene copolymer, styrene-isoprene copolymer, acrylonitrile-butadiene copolymer or the like. Also, these polymers can be hydrogenated in a minor/major part of intramolecular double bonds thereof. It is particularly preferable to use polybutadiene or styrene-butadiene copolymer as a polymer component.

[0025] As needed, an additive, a lubricant, a flame retardant, an antistatic agent, a pigment/dyestuff, a foam nucleus and an ultraviolet stabilizer can be added to the resin. The form of the expandable particle has an influence on particle fusability in molding the expandable particles in the mold. The fusability increases as sphericity of the particle increases. This is because the particles expand isotropically in molding to constrict each other, thus inhibiting irregularity of unfilled spaces between the particles and making remaining voids between the particles smaller. The obtained expandable particle of the present invention is spherical, the sphericity thereof being from 1.0 to 1.3.

[0026] The preferable range of diameter of the expandable particle of the present invention is from 0.5 to 3.0 mm. When the particle diameter being smaller than 0.5 mm, the die nozzle is likely to clog up while extruding the resin, so that the production will difficult. On the other hand, when the particle diameter is larger than 3.0 mm, temperature and time are needed in impregnation for forming the particle into the spherical shape. Further, when the particle is made expandable to be used in molding, it is impossible to fill the particles in minute parts of the mold. The more preferable range of particle diameter is from 0.6 to 2.0 mm.

[0027] In the extruder for the polystyrene-based resin containing conjugated diene-based polymer component of the present invention, the diameter of the die land preferably ranges from 0.5 to 2.5 mm. The more preferable range of diameter is from 0.6 to 1.5 mm. A shorter die land will give a larger swell, while a longer die land will be likely to get the nozzle clogged. The more preferable range of the die land is from 5 to 12

mm.

[0028] When extruding the resin, the preferable range of temperature of the resin is from 220 to 260 deg. C and the preferable range of pressure of the resin is from 90 to 120 kgf/cm^2. A larger feeding velocity of the resin will give a higher resin pressure, while a smaller velocity will supply only insufficient heat to make the nozzle be easily clogged. The preferable range of temperature of water supplied to the die face is from 40 to 90 deg. C. When the temperature being lower than 40 deg. C, the resin is likely to clog up since the die face is excessively cooled off. On the other hand, when the temperature is higher than 90 deg. C, the hot water is difficult to be handled due to steam. The more preferable temperature range is from 50 to 70 deg. C.

[0029] The shear rate of the resin at the die land part and the apparent viscosity are obtained in the following manner. Provided that the diameter of the land part is d (cm), the supply of resin per a land is q (gr/sec) and the resin density at the die temperature is n (gr/cm^3), the resin line velocity v is represented by $v = (4*q)/(\pi*n*d^2)$.

[0030] In this state, the shear rate at the land part γ (1/sec) is calculated by the equation of $\gamma = (8v)/d$. In addition, the characteristic between the shear rate of the resin and the apparent viscosity at each temperature is obtained in advance to obtain the apparent viscosity at the land part using the die land temperature and the shear rate of the resin.

[0031] In the present invention, the method for obtaining an expandable resin particle is not limited as long as it is an underwater suspension impregnation method. In other words, various known methods can be applied, in which a polystyrene-based resin particle containing rubber component obtained as described above is put into a pressure-proof container provided with a stirrer, stirred and dissolved in the presence of suspension stabilizers and surface acting agents in an aqueous medium to be impregnated with a blowing agent. The inside of the container can be heated if necessary. After the impregnation, the particle is cooled to the ambient temperature, thereafter the blowing agent remaining in the container is removed and the particle is taken out under the ambient

temperature to obtain an expandable particle.

[0031] Volatile blowing agents having boiling temperature ranging from – 30 to +100 deg. C can be used in the present invention. Such agents includes, for example, aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane and petroleum ether, cyclic aliphatic hydrocarbons such as cyclopentane and dichlorohexane, and halogenated hydrocarbons such as chloromethane, chloroethane, bromomethane, dichlorodifluoromethane and 1,2-dichlorotetrafluoroethane, monochlorotrifluoroethane. Pentane and butane are particularly preferred blowing agents.

[0033] In addition to the above-mentioned blowing agent, a surface active agent such as dodecylbenzenesulfonate and laurylalcoxysulfonate, a dispersing agent such as magnesium carbonate, magnesium sulfate, sodium pyrophosphate, calcium carbonate, talc and tricalcium phosphate, and a solvent such as a toluene and xylene can be mixed with the aqueous medium.

[0034] The blowing agent preferably impregnates the area of 4 to 12 weight part per 100 weight part of resin. When the area is smaller than 4 part, it becomes difficult to expand the expandable particle at higher rate of expansion. On the other hand, when the area is larger than 12 weight part, it is difficult to control the rate of expansion. The more blowing agent is added, the higher the expansion rate becomes. The more preferable range of the impregnated area of the blowing agent is 5 to 11 weight part. In order to shorten the impregnation time in the blowing agent and form the resin particle into sphericity, the inside of the container is preferably heated to 40 to 130 deg. C. The heating temperature is preferably chosen in consideration of pressure capacity of the container, blocking property of the resin particle and the impregnation time.

[0035] The process of obtaining an expanded particle and a molded foamed article from the obtained expandable particle can be carried out in, but not limited to, a commonly used method. For example, the expandable particle can be expanded with steam by a known expanding machine for expandable polystyrene beads to give a expanded particle with at an

expansion rate of 5 to 100. As an example of conditions of expansion, heating temperature and expansion retention time at this temperature can be set to 95 to 104 deg. C and 10 to 150 seconds, respectively. The expanded particle is further exposed to the air to allow the air to penetrate into the expanded particle. The expanded resin particle thus obtained is heated with steam in a mold having a small hole/slit provided inside a known automatic molding machine for expandable polystyrene beads and fused to each other to become a molded foamed article.

Brief description of the drawings

Fig. 1 is a schematic diagram showing an extruder and a device for underwater hot-cut.

Fig. 2 is a schematic diagram showing a cross-sectional constitution of the die of the extruder.

Description of preferred embodiments

[0036] The present invention will be described below in detail with reference to preferred examples, but it is not limited by these exampless in any way. The properties of the particles in the exampless and the comparative examples are measured and evaluated in the following manner.

[0037]

(1) Sphericity of the particle

Measurement method: the maximum width H is measured between two parallel lines which sandwich the particle on the projection plane. Although the value H varies as the direction of projection changes, provided that the maximal value of the varying H is H1 and the minimal value is H2, sphericity of the particle is obtained by the following formula.

$U = H1/H2$

Evaluation:

symbol	value of U
E (excellent)	1.00 or more and less than 1.15
G (good)	1.15 or more and less than 1.30
F (fair)	1.30 or more and less than 1.60
P (poor)	1.60 or more

[0038]

(2) rate of particle blocking

Measurement method: the weight (W1) of the whole particles obtained by the process of impregnation of the blowing agent and the weight (W2) of the agglomerated particles consisting of at least two particles are obtained, and the rate of particle blocking (B) is obtained by the following formula.

$B = (W2/W1)*100$

Evaluation:

symbol	value of U
E (excellent)	0.0 % or more and less than0.5 %
G (good)	0.5 or more and less than 1.5
F (fair)	1.5 or more and less than 4.0
P (poor)	4.0 or more

[0040]

(3) particle diameter

Measurement method: the average weight per a particle is calculated from the weights of 100 particles that have been randomly chosen. The average weight is divided by the resin density to give the volume. The particle diameter is calculated with assuming that the particle is a perfectly spherical.

[0041]

(4) limiting viscosity of the polystyrene based component phase

Measurement method: 1 g of resin is added to 20 ml of solvent comprising methylethylketone and methanol at the capacity ratio of 9/1, shaken up and subjected to centrifugal separation. The resin component is precipitated from the supernatant liquid using methanol. The viscosity of the toluene solution of the obtained resin having density of 0.5 g/dl is measured and the converted viscosity ($\eta sp/c$) at 30 deg. C is obtained on the basis of the measured viscosity.

[0042]

(5) content of the blowing agent

Measurement method: the expandable particle is heated on a heating plate with the temperature of 200 deg. C, and the content of the blowing agent is obtained from decrease in weight.

[0043]

(6) true density of the expanded particle

Measurement method: the true density of the expanded particle ρ (g/cm^3) is obtained by the following formula.

$\rho = W/V$

where W is the weight of the expanded particle (g), and V is the volume of the expanded particle obtained by the submerging method (cm^3).

[0044]

(7) powder density of the molded foamed article

Measurement method: the powder density of the molded foamed article D (g/cm^3) is obtained using the following formula based on Japanese Industrial Standards K6767.

$D = G/V$

Where G is the weight of the molded formed article (g), and V is the volume of the molded foamed article (cm^3).

[0045]

(8) rate of fused particle contained in the molded foamed article

Measurement method: the rate of fused particle contained in the molded foamed article Y (%) is obtained by the following formula, where among the particles being exposed on the fracture surface of the molded foamed article, N1 is the number of particles that are broken to the inside, and N2 is the number of particles that are not broken to the inside and exposed on the surfaces thereof.

$Y = \{(N1)/(N1 + N2)\} * 100$

Evaluation:

symbol	value of Y
E (excellent)	90 % or more and less than 100 %
G (good)	80 or more and less than 90
F (fair)	70 or more and less than 80
P (poor)	less than 70

[0046]

(9) tensile break strength of the molded article

Measurement method: measurement is carried out based on Japanese

Industrial Standards K6767.

Evaluation:

Symbol	value of tensile break strength
E (excellent)	3.5 kgf/cm^2 or more
G (good)	3.0 or more and less than 3.5
F (fair)	2.5 or more and less than 3.0
P (poor)	less than2.5

[0047]

(10) crack resistant drop height of the molded article

Measurement method: an L-shape molded foamed article with 20 mm thickness, 70mm length and breadth and 60mm width is prepared. The molded article is placed on a mold in the shape of a right-angled triangle pole whose right-angle portion is set on the top, in such a way that the right-angle portion of the molded article is placed on the right-angle edge of the mold. Upon the molded article is further placed an A flute corrugated board. A weight in the shape of a flat plate having the weight of 2.43 kg is fallen from a height H (cm) onto the molded article to measure the minimal height Hmin at which the molded article is broken at its edge. Hmin measured in this way is the crack resistant drop height T (cm) of the molded article.

Evaluation:

symbol	value of T
E (excellent)	11.0cm or more
G (good)	9.5 or more and less than 11.0
F (fair)	8.0 or more and less than 9.5
P (poor)	less than 8.0

[0048] (Example 1) Rubber component-containing polystyrene having 9 wt % of butadiene and a limiting viscosity of the polystyrene phase of 0.7 (manufactured by Asahi Kasei Corporation) is mixed with 0.1 part of ethyrenebisstearoamide and 0.1 part of amide stearate. The mixture is heat-melted in an extruder at 240 to 250 deg. C, and the melt is kneaded. The melted and kneaded resin is extruded from a die head provided with a

die land with a diameter of 0.7 mm and five dozens extruding holes with a diameter of 0.7 mm into circulating water at 60 deg. C to be cut simultaneously by the die face using a rotating blade. The cut particle is pulled out with circulating water and subjected to centrifugal dehydration and drying process to make a spherical particle having the average diameter of 1.1 mm. The shear rate of the resin at the die land part is 4,500 (1/sec.), and the apparent viscosity is 320 poise.

[0049] 100 g of the obtained particles are put inside a pressure tight container of 0.5 L provided with a stirrer together with 130 g of water, 5 g of magnesium carbonate powder and 0.01 g of sodium dodecylbenzenesulfonate. 14 g of mixed pentane that contains i-pentane and n-pentane at the weight ratio of 50/50 as a blowing agent is further added. After tightly closing the case, while the mixture is stirred at 600 rpm, it is heated to 120 deg. C in 30 minutes and maintained at 120 deg. C for six hours. Then the case is cooled off to obtain expandable particles. The rate of particle blocking in the container is 0.4 %. The sphericity of the obtained particles without blocking is 1.11. The content of the blowing agent in the obtained particles are 7.4 weight part per 100 weight part of the resin.

[0050] The obtained particles are expanded by steam heating to become expanded particles with true density of 0.029 g/cm^3, which are molded in a mold at the steam pressure of 0.8 kgf/cm^2 to obtain a molded planner article having dimensions of 300*300*50 mm. The powder density of the obtained molded article is 0.020 g/cm^3, and the rate of fused particles is 92 %, and the tensile break strength is 3.6 kgf/cm^2. The crack resistance of the molded article as measured by the height of crack resistance is 11.0 cm, which is quite a good value.

[0051] (Example 2) Expandable particles are obtained in the same process as in Example 1 except that the amounts of the blowing agent to be mixed in are 12 parts and 17 parts in the process of impregnation of the blowing agent. The contents of the blowing agent contained in the obtained particles are 6.5 weight part and 9.2 weight part respectively. The characteristics of the obtained expandable particles are shown in Table 1

(where polystyrene containing rubber component is abbreviated as HIPS and conditions of underwater cutting is abbreviated as UWC conditions). The performances of the molded article obtained by expanding and molding the expandable particles under the same conditions as in Example 1 are shown in Table 3.

[0052] (Example 3) Expandable particles are obtained in the same process as in Example 1 except that the shear rate at the die land part is set to 2,900, 6,100 and 8,500 (1/sec.), and the apparent viscosity to 610, 220 and 180 poise respectively in the process of extruding the polystyrene containing butadiene component, by controlling the die temperature and the rate of resin supply. The characteristics of the obtained expandable particles are shown in Table 1. The performances of the molded article obtained by expanding and molding the expandable particles under the same conditions as in Example 1 are shown in Table 3.

[0053] (Example 4) Expandable particles are obtained in the same process as in Example 1except that the die land diameter (as well as the extruding hole diameter) is 1.2 mm and 2.0 mm. The shear rate at the die land part is 4,000 and 3,500 (1/sec.), and the apparent viscosity is 310 and 400 poise respectively. The characteristics of the obtained expandable particles are shown in Table 1, while the performances of the molded article are shown in Table 3.

[0054] (Example 5) Expandable particles are obtained in the same process as in embodiment 1except that the content of butadiene component in the polystyrene containing butadiene content is 5 % and 12 % (manufactured by Asahi Kasei Corporation). The shear rate at the die land part is 4,500 (1/sec.), while the apparent viscosity is 290 and 360 poise respectively. The characteristics of the obtained expandable particles are shown in Table 1, while the performances of the molded article are shown in Table 3.

[0055] (Comparative Example 1) Expandable particles are obtained in the same process as in Example 1except that high-impact polystyrene (manufactured by Asahi Kasei Corporation) containing 9 % of butadiene component is used, and the shear rate of resin at the die land part is 2,200 and 11,000 (1/sec.), and the apparent viscosity is 750 and 140 poise

respectively. The characteristics of the obtained expandable particles are shown in Table 2. The sphericity as well as the rate of particle blocking is not comparable. The performances of the molded article obtained by expanding and molding the expandable particles under the same conditions as in Example 1 are shown in Table 4. The crack resistance is lower than the molded article of Example 1.

[0056] (Comparative Example 2) Expandable particles are obtained in the same process as in Comparative Example 1except that impregnation of the blowing agent is carried out at 120 deg. C for 12 hours. The characteristics of the obtained expandable particles are shown in Table 2. Although the sphericity of the expandable particle is improved, the rate of particle blocking is still large. The performances of the molded article obtained by expanding and molding the expandable particles under the conditions as shown in embodiment 1.

[0057] (Comparative Example 3) Expandable particles are obtained in the same process as in Example 1, wherein the die land diameter (as well as the extruding hole diameter) is 2.6 and 0.4 mm. The shear rate at the die land part is 3,200 and 8,500 (1/sec.), while the apparent viscosity is 510 and 190 poise respectively. In the case of using the die land diameter of 0.4 mm, the die nozzle stops up easily, making it difficult to continue extrusion of the resin. The expandable particles are dispersed in the aqueous medium to be impregnated with the blowing agent in the same way as in Example 1. The characteristics of the obtained expandable particles are shown in Table 2. The performances of the molded article obtained by expanding and molding the expandable particles under the same conditions as in Example 1 are shown in Table 4.

[0058] (Comparative Example 4) Expandable particles are obtained in the same process of Example 1except that a HIPS is used whose content of rubber component in the polystyrene containing butadiene component is 6 % and 15 %, and whose limiting viscosity is 0.57 and 0.92 respectively, the conditions of extrusion being shown in Table 2. The characteristics of the obtained expandable particles are shown in Table 2, while the performances of the molded article are shown in Table 4.

[0059] (Comparative Example 5) A pellet in a cylindrical shape having the diameter of 1.0 mm and the length of 1.2 mm is obtained by extruding from an expanding machine the mixture as used in Example 1 containing HIPS and the additive agents. This pellet is put into the impregnation container in the same way as in Example 1 to be impregnated at 120 deg. C for 6 and 12 hours to obtain expandable particles. The characteristics of the obtained particles are shown in Table 2. The performances of the molded article are shown in Table 4.

[0060] (Comparative Example 6) A polystyrene containing 2 % of butadiene component is prepared by diluting a polystyrene containing 9 % of butadiene component (manufactured by Asahi Kasei Corporation) with polystyrene. Expandable particles are obtained in the same process of Example 1except that resin of this polystyrene is used, and the shear rate of the resin at the die land part is 4,500 and 8,500 (1/sec.), and the apparent viscosity is 360 and 190 poise respectively. The characteristics of the obtained expandable particles are shown in Table 2, while the performances of the molded article obtained by expanding and molding the expandable particles under the same conditions as in Example 1 are shown in Table 3.

[0061] Table 1

	No.	Rubber content in HIPS (wt%)	Limiting viscosity of HIPS	UWC condition		Suspension impregnation condition	Properties of expandable particle		
				Shear rate (1/sec)	Apparent viscosity (poise)	Temp. (deg. C) x Time (h)	Blocking rate	Sphericity of particle	Particle diameter (mm)
Example 1	1	9	0.70	4500	320	120 x 6	E 0.4 %	E 1.11	1.1
Example 2	2	9	0.70	4500	320	120 x 6	E 0.3	E 1.11	1.1
	3	9	0.70	4500	320	120 x 6	G 1.0	E 1.10	1.1
Example 3	4	9	0.70	2900	610	120 x 6	G 0.8	G 1.18	1.0
	5	9	0.70	6100	220	120 x 6	G 1.1	G 1.19	1.1
	6	9	0.70	8500	180	120 x 6	G 1.3	G 1.22	1.2
Example 4	7	9	0.70	4000	310	120 x 6	E 0.4	E 1.13	1.6
	8	9	0.70	3500	400	120 x 6	G 1.0	G 1.16	2.5
Example 5	9	5	0.83	4500	290	120 x 6	E 0.4	E 1.12	1.1
	10	12	0.65	4500	360	120 x 6	E 0.4	E 1.14	1.1

[0062] Table 2

	No.	Rubber content in HIPS (wt%)	Limiting viscosity of HIPS	UWC condition		Suspension impregnation condition	Properties of expandable particle		
				Shear rate (1/sec)	Apparent viscosity (poise)	Temp. (deg. C) x Time (h)	Blocking rate	Sphericity of particle	Particle diameter (mm)
Comparative Example 1	11	9	0.70	2200	750	120 x 6	P 4.4	F 1.42	1.1
	12	9	0.70	11000	140	120 x 6	F 3.2	F 1.33	1.1
Comparative Example 2	13	9	0.70	2200	750	120 x 12	P 5.8	F 1.25	1.1
	14	9	0.70	11000	140	120 x 12	P 5.2	G 1.20	1.1
Comparative Example 3	15	9	0.70	3200	510	120 x 6	F 3.5	F 1.39	3.2
	16	9	0.57	8500	190	120 x 6	F 2.8	F 1.32	0.5
Comparative Example 4	17	6	0.92	4200	430	120 x 6	F 2.6	F 1.31	1.2
	18	15	0.70	4700	350	120 x 6	F 2.8	F 1.36	1.3
Comparative Example 5	19	6	0.70	Strand cut		120 x 6	P 8.5 %	F 1.50	1.3
	20	9	0.88	Strand cut		120 x 12	P 10.8 %	F 1.31	1.3
Comparative Example 6	21	2	0.88	4500	360	120 x 6	F 3.6	F 1.38	1.1
	22	2	0.65	8500	190	120 x 6	F 2.5	G 1.29	1.1

[0063] Table 3

	No.	Properties of article		
		Fusing rate (%)	Tensile strength (kgf/cm^2)	Crack resistant drop height (cm)
Example 1	1	E 92	E 3.6	E 11.0
Example 2	2	E 90	E 3.5	E 11.0
	3	E 91	E 3.6	E 11.0
Example 3	4	G 87	G 3.4	G 10.5
	5	G 86	G 3.3	G 10.5
	6	G 85	G 3.2	G 10.0
Example 4	7	E 90	E 3.5	E 11.0
	8	E 90	E 3.5	E 11.0
Example 5	9	E 91	E 3.5	G 9.5
	10	G 89	G 3.4	E 11.0

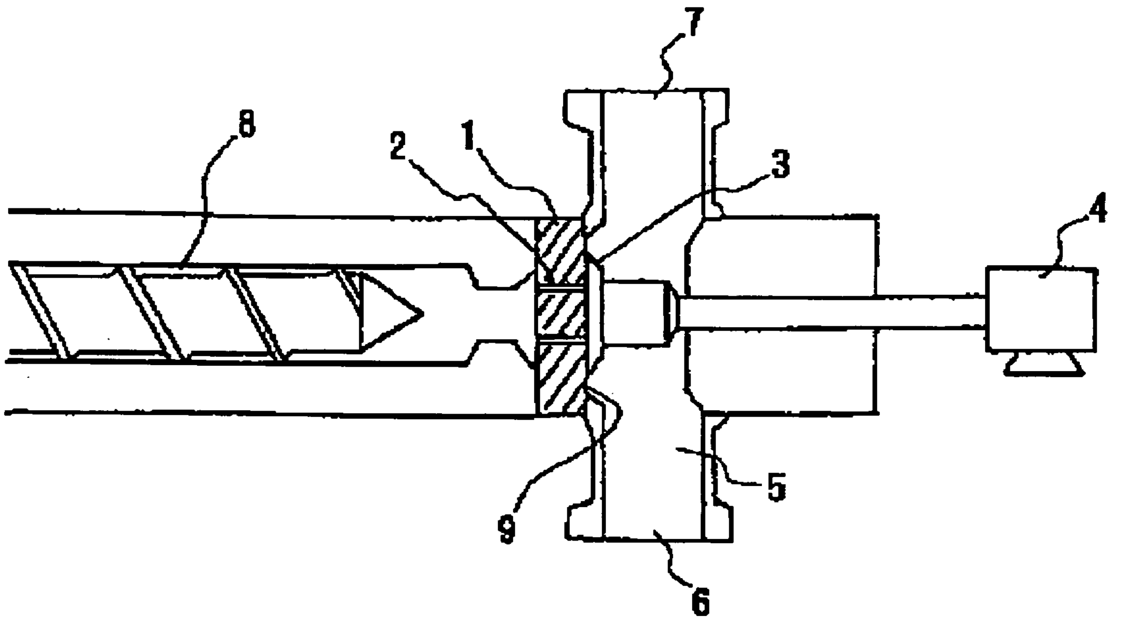
[0064] Table 4

	No.	Properties of article		
		Fusing rate (%)	Tensile strength (kgf/cm^2)	Crack resistant drop height (cm)
Comparative Example 1	11	F 74	P 2.4	F 8.5
	12	F 77	F 2.5	F 8.5
Comparative Example 2	13	F 77	G 3.2	F 8.5
	14	G 82	G 3.3	F 9.0
Comparative Example 3	15	F 75	G 3.1	F 8.5
	16	F 74	F 2.5	F 8.5
Comparative Example 4	17	F 76	G 3.2	F 8.5
	18	F 72	P 2.4	F 8.0
Comparative Example 5	19	F 72	F 2.5	F 8.5
	20	F 79	G 3.2	F 8.5
Comparative Example 6	21	F 75	G 3.4	P 6.0
	22	F 79	G 3.3	P 6.5

[0065] The effect of the invention: according to the present invention, spherical expandable particles of polystyrene resin containing conjugated diene-based polymer component can be produced efficiently within a short length of impregnation time without causing blocking. A molded article obtained by expanding and molding the obtained expandable resin particles exhibits excellent crack resistance.

1	die head
2	die nozzle
3	cutting blade
4	motor
5	cutter box
6	water inlet
7	water outlet
8	screw of the extruding machine
9	die face
10	die land
11	taper part
12	die extruding hole

[FIG. 1]



[FIG. 2]